

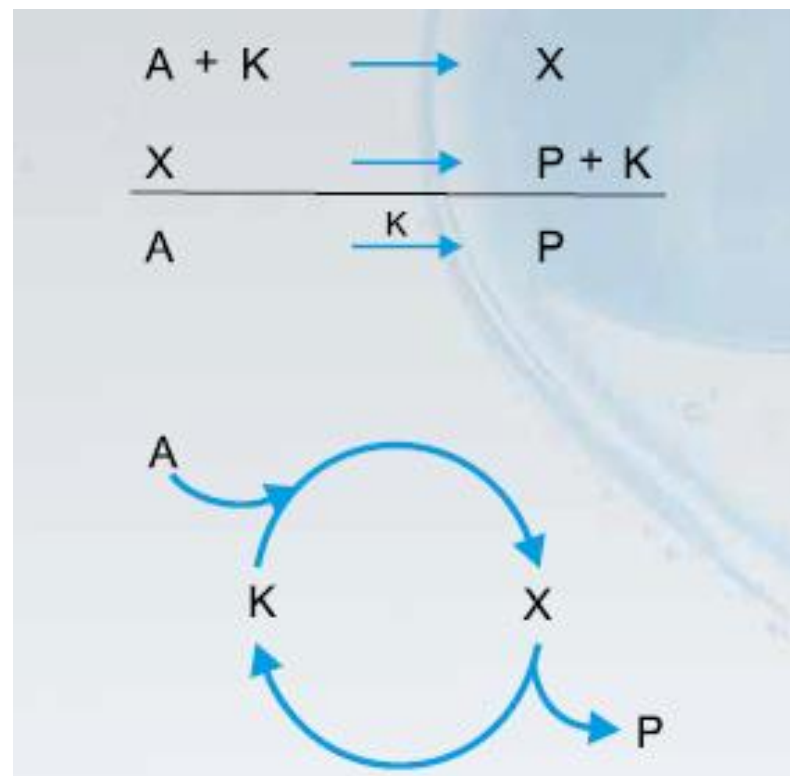
Lecture 6 Catalytic processes. Homogeneous and heterogeneous catalysis.

Many reactions are too slow for technical applications at ambient temperature because the required activation energy is very high. Catalysts lower the required activation energy and accelerate the chemical reaction. Thus, some reactions would not be possible without a catalyst reducing the energy required for production.

Catalysis has been defined as the process by which chemical reaction rates are altered by the addition of a substance (**the catalyst**) that is not itself changed during the chemical reaction.

Catalysts are usually used so that chemical reactions can occur at temperatures and pressures low enough for producers to use economically priced equipment or to ensure that the rate of production of a desired product is greater than the rates of production of undesirable by-products. Catalysis-based chemical synthesis accounts for 60 percent of today's chemical products and is a factor in 90 percent of current chemical processes.

In the simple case of the reaction of a reactant *A* to a product *P* by means of a catalyst *K*, one can imagine that the catalysis occurs via an intermediate product *X*. *The* reactant and the catalyst thus first form an intermediate product. In a second step, the catalyst is released and the intermediate product is converted to form the product *P*. The catalyst is unchanged after the reaction and is available again for further reactions. One possible explanation of catalysis is the theory of the transition state. This theory assumes that the reactants involved in the reaction have to cross an energy barrier for the reaction to take place.

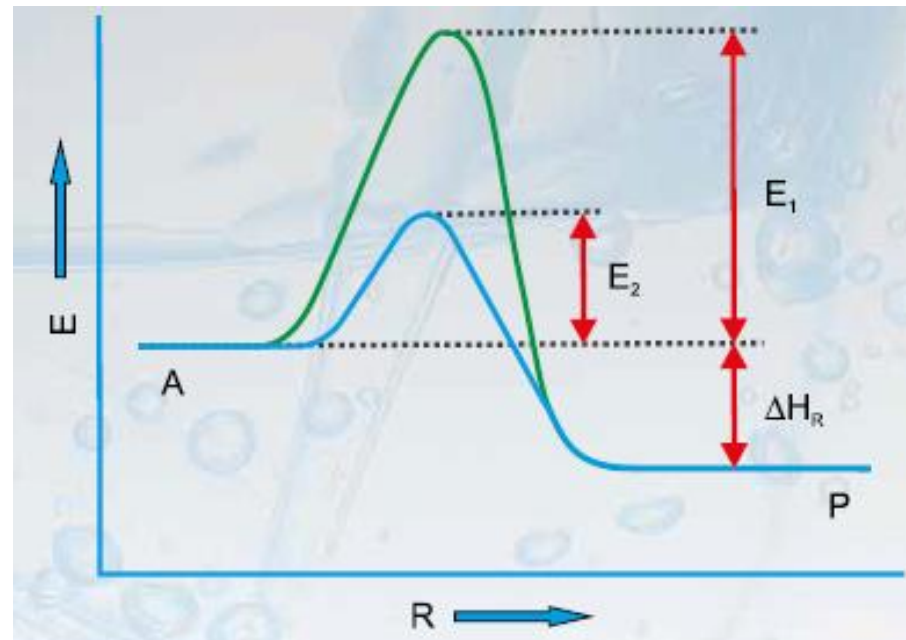


Reaction schematic of a simple catalytic reaction as a schematic (top) and cycle (bottom):

*A is reactant, K is catalyst,
X is intermediate product, P is product*

How Does a Catalyst Work?

The molecular state at the maximum of the energy barrier *E1* is referred to as *activated* complex. The products form directly from this molecular state. During catalysis, the activated complex is formed from the reactants and the catalyst. The energy *E2*, which is required to form the complex with the catalyst, is lower than the energy *E1* which would be required without the catalyst. This lower energy requirement means that a larger number of reactants react per time unit to form products, i.e. the reaction rate is higher.



Energy change with and without catalyst (exothermic):

E is energy, R is reaction coordinate, E_1 is energy required to form an activated complex without catalyst, E_2 energy required to form an activated complex with catalyst, ΔH_R reaction enthalpy

Types of catalytic reactions

Catalysts can be divided into two main types - **heterogeneous** and **homogeneous**.

Homogeneous catalysis

The catalyst and the starting substances of the chemical reaction are in the same phase. This means that the reaction takes place either in the liquid or in the gaseous phase. In the liquid phase, the properties of the solvent (e.g. viscosity) also influence the reaction rate in addition to the type of reactants and catalyst.

Heterogeneous catalysis

The catalyst is in the solid phase in most cases. The starting substances of the reaction are in the liquid or gaseous phase. In addition to the actual chemical reaction between reactants and catalyst, processes such as diffusion inside the solid catalyst and sorption processes have a significant influence on the reaction rate.

Base stages of heterogeneous catalysis

I. One or more of the reactants are adsorbed on to the surface of the catalyst at active sites. Adsorption is where something sticks to a surface. It isn't the same as absorption where one substance is taken up within the structure of another. An active site is a part of the surface which is particularly good at adsorbing things and helping them to react.

II. There is some sort of interaction between the surface of the catalyst and the reactant molecules which makes them more reactive. This might involve an actual reaction with the surface, or some weakening of the bonds in the attached molecules.

III. The reaction happens. At this stage, both of the reactant molecules might be attached to the surface, or one might be attached and hit by the other one moving freely in the gas or liquid.

IV. The product molecules are desorbed. Desorption simply means that the product molecules break away. This leaves the active site available for a new set of molecules to attach to and react.

- A good catalyst needs to adsorb the reactant molecules strongly enough for them to react, but not so strongly that the product molecules stick more or less permanently to the surface.
- Silver, for example, isn't a good catalyst because it doesn't form strong enough attachments with reactant molecules. Tungsten, on the other hand, isn't a good catalyst because it adsorbs too strongly.
- Metals like platinum and nickel make good catalysts because they adsorb strongly enough to hold and activate the reactants, but not so strongly that the products can't break away.

General features:

Heterogeneous

Readily separated ✓
Readily recycled / regenerated ✓
Long-lived ✓
Cheap ✓

Lower rates (diffusion limited) ✗
Sensitive to poisons ✗
Lower selectivity ✗
High energy process ✗
Poor mechanistic understanding ✗

Homogeneous

Difficult to separate ✗
Difficult to recover ✗
Short service life ✗
Expensive ✗

Very high rates ✓
Robust to poisons ✓
Highly selective ✓
Mild conditions ✓
Mechanisms often known ✓

Heterogeneous catalysts are used in refining / bulk chemical syntheses much more than in fine chemicals and pharmaceuticals (which tend to use homogeneous catalysis).

Examples of heterogeneous catalysis

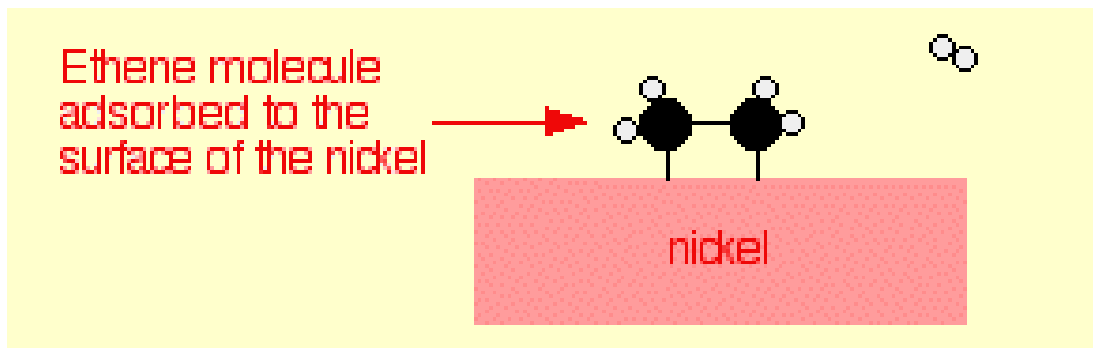
The hydrogenation of a carbon-carbon double bond.

The simplest example of this is the reaction between ethene and hydrogen in the presence of a nickel catalyst.

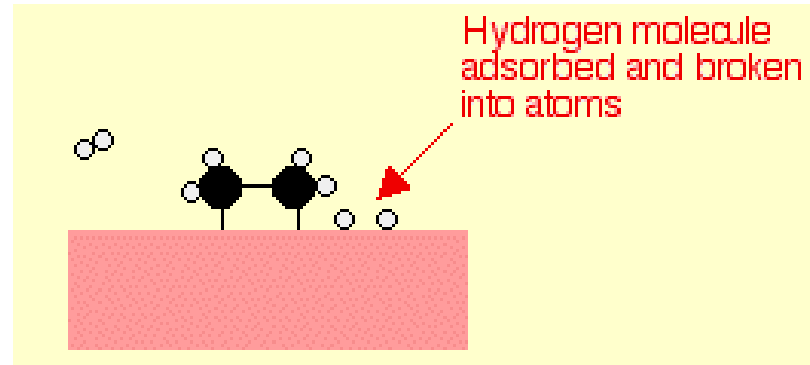
In practice, this is a pointless reaction, because you are converting the extremely useful ethene into the relatively useless ethane. However, the same reaction will happen with any compound containing a carbon-carbon double bond.

One important industrial use is in the hydrogenation of vegetable oils to make margarine, which also involves reacting a carbon-carbon double bond in the vegetable oil with hydrogen in the presence of a nickel catalyst.

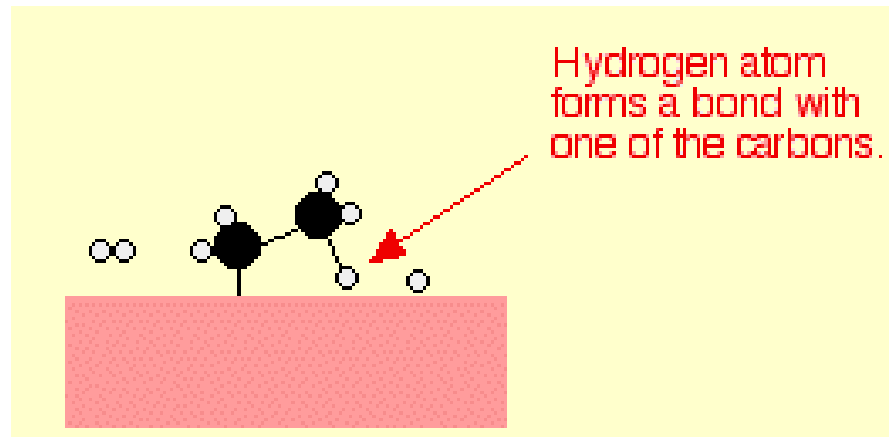
Ethene molecules are adsorbed on the surface of the nickel. The double bond between the carbon atoms breaks and the electrons are used to bond it to the nickel surface.



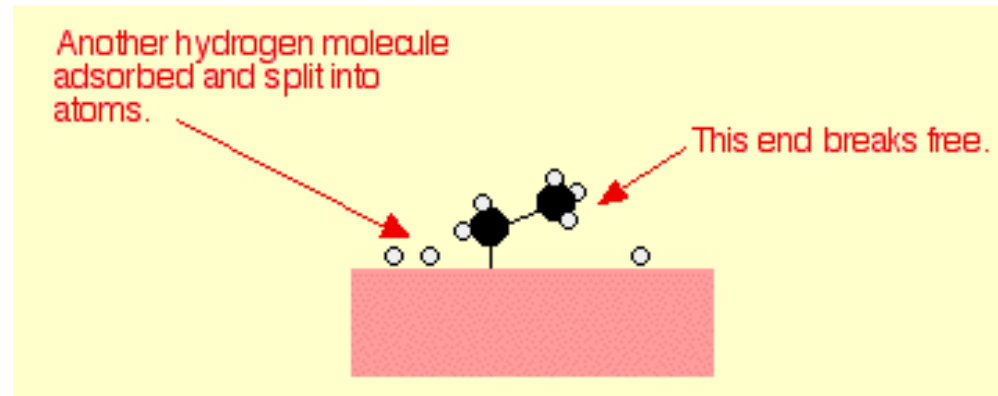
Hydrogen molecules are also adsorbed on to the surface of the nickel. When this happens, the hydrogen molecules are broken into atoms. These can move around on the surface of the nickel.



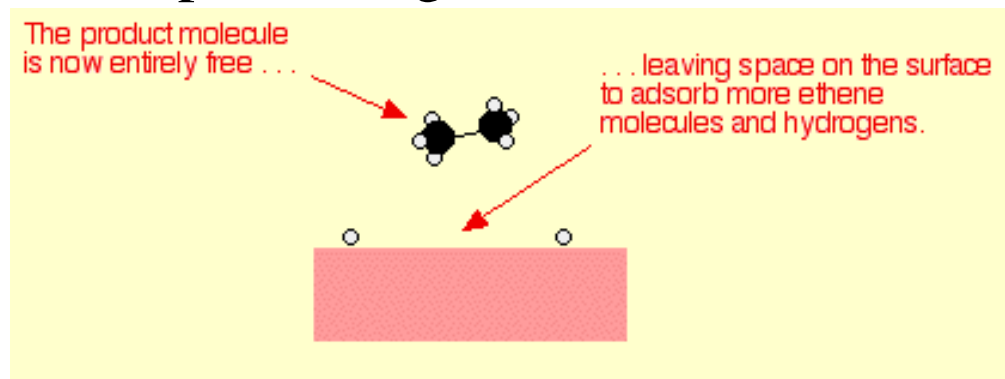
If a hydrogen atom diffuses close to one of the bonded carbons, the bond between the carbon and the nickel is replaced by one between the carbon and hydrogen.



That end of the original ethene now breaks free of the surface, and eventually the same thing will happen at the other end.



As before, one of the hydrogen atoms forms a bond with the carbon, and that end also breaks free. There is now space on the surface of the nickel for new reactant molecules to go through the whole process again.



Types of catalysts

Types of catalysts are listed below:

Positive catalysts:

A catalyst which increases the rate of reaction is called positive catalyst. Such catalyst decreases activation energy by accepting a smaller path, so rate of reaction is increased.



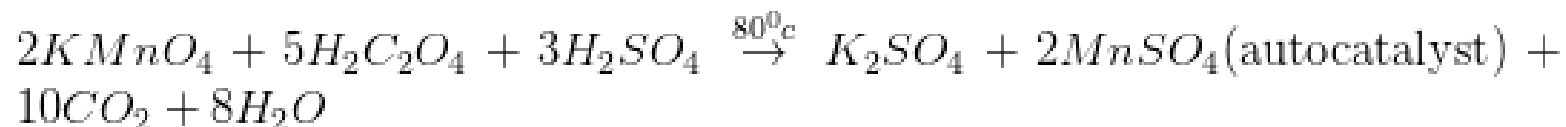
Negative catalysts (Inhibitors):

A catalyst which decreases or retards the rate of reaction is called negative catalysts. It is because negative catalyst increase activation energy by taking a longer alternative path.



Auto-catalysts:

When one of the products formed in the reaction acts as a catalyst is known as auto-catalyst.



Induced catalyst:

The substance which influences the speed of other reaction, which is not possible under ordinary conditions, is known as induced catalyst.

E. g. Sodium sulphite solution readily oxidises in air, but sodium arsenite solution does not oxidise by passing air in the solution. When both these solutions are mixed and air is passed then both the substances get oxidised.

